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Theory of size effects in ferroelectric ceramic thin films on metal substrates

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Abstract The aim of this paper is to show how a Landau thermodynamic theory might be utilized to study size effects in ferroelectric thin films on metal substrates via reflectivity measurements that could be carried out with terahertz radiation, particularly in the far-infrared region. The approach taken is to minimize a Landau free energy functional that includes a gradient term to describe the size effects. Landau-Khalatnikov equations together with Maxwell's equations for the electromagnetic field are then solved simultaneously to describe how the radiation interacts with the film. From this reflectivity curves can be calculated and related to experimental studies. Attention is paid to how the metal substrate can influence the reflectivity curves compared to free standing films without substrates. The significance of the work lies in the fact that ferroelectric ceramic thin films are becoming of increasing technological importance, and films on metal substrates such as electrodes are of obvious relevance to applications such as memory devices which rely on applied electric fields to change the polarization direction. The main conclusion is that terahertz wave measurements in the far-infrared provide an informative and sensitive probe of the size effects and substrate influence.

Keywords Ferroelectrics · Terahertz · Far infrared · Nanoscale · Thin films · Size effects

1 Introduction

The physical properties of ferroelectric nanostructures are found to be different from those of bulk materials [1]. Size effects in ferroelectric thin films and nanoparticles in particular, are of much interest because of current applications in memory devices [2]. Chew et al. [3, 4] have studied the influence of the polarization on the dynamic properties of free standing ferroelectric thin films within the framework of LDG theory by using Landau-Khalatnikov equations to model the dynamics. This work suggests that terahertz radiation particularly in the far infrared (FIR) is a sensitive probe of size effects in ferroelectric thin films.

Here a similar approach to that of Chew et al. [3, 4] will be used. The difference is that now one side of the thin film is attached to a metal substrate. Assuming this to be of very high conductivity, at the ferroelectric-metal interface most of the radiation, due to an electromagnetic field penetrating from the opposite side, will be reflected back into the film and the transmission coefficient will be close to zero. The main aim of this paper is to find out how the reflection coefficient behaves as a function of frequency for the ferroelectric film on a metal substrate and to investigate whether useful information about the size effects can still be measured by terahertz wave reflection. The behaviour is expected to be quite different from the free standing films studied by Chew et al. [3, 4] because of the strong reflection at the ferroelectric-metal interface.

2 Formalism

The starting point is the Gibbs free energy per unit area for a ferroelectric film of thickness L and polarization P

$$F/S = \int_{-L}^{0} ((1/2)AP^2 + (1/4)BP^4 + (C/2)(dP/dz)^2 - \vec{E}\cdot\vec{P})\,dz + (C/2)(P^2(-L)/\delta_1 + P^2(0)/\delta_2), \quad (1)$$

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where the integrand is the Landau free-energy density for a second order transition with $A = a(T - T_0)$ and $B > 0$ (for simplicity first order transitions are not considered here); T_0 is the Curie temperature of the bulk material and the term $\vec{E} \cdot \vec{P}$ describes the coupling to an incident electric field. The C gradient term in the integrand represents the free-energy cost of spatial variations in P. To find P_0, the equilibrium value of P, it is necessary to minimize the free energy in Eq. (1) with $\vec{E} = 0$ using the calculus of variations; this leads to the Euler-Lagrange equation for P,

$$C\frac{d^2P}{dz^2} - AP - BP^3 = 0. \tag{2}$$

The boundary conditions, which come from the second term in Eq. (1), are

$$dP/dz - P/\delta_1 = 0, \quad \text{at } z = -L, \tag{3}$$

$$dP/dz + P/\delta_2 = 0, \quad \text{at } z = 0. \tag{4}$$

The extrapolation lengths δ_1 and δ_2 are allowed to be different at each boundary since the interfaces are different with $z = -L$ chosen to be the boundary with the metal and $z = 0$ the boundary with the air (assumed to behave like a vacuum) from which the E field will be incident for the dynamical equations below. For $\delta_1, \delta_2 > 0$ it can be seen from Eqs. (3) and (4) that the polarization turns down at the surfaces, so that the values there are smaller then the bulk polarization; consequently the critical temperature of the film T_c is smaller than T_0. Negative extrapolation lengths imply an upturn of P at the corresponding surface, but in this paper only positive values will be considered.

Equation (2) subject to conditions (3) and (4) can be solved to find $P(z)$ in terms of elliptic functions. For $\delta_1 = \delta_2$ this has been done in Refs. [5] and [6]. Here the solution needs to take $\delta_1 \neq \delta_2$ in to account. The solution [5] already given for $\delta_1 = \delta_2$ in terms of elliptic function sn is still valid since G, the constant of integration that appears in this solution, is determined by boundary conditions (3) and (4). The determination of G for these conditions requires finding a value that simultaneously satisfies both boundary conditions. This can be done in a two-step numerical process [7].

The dynamic coupling of the time dependent electromagnetic field E is described using a Landau-Khalatnikov equation of motion,

$$m\frac{\partial^2 P}{\partial t^2} + \gamma\frac{\partial P}{\partial t} = -\frac{\delta F}{\delta P} = -\left(C\frac{d^2P}{dz^2} - AP - BP^3\right), \tag{5}$$

given in a form suitable for damped oscillatory systems since this describes the soft mode observed in many displacive ferroelectrics such as $BaTiO_2$ (later we will choose parameter values for $BaTiO_2$ for illustration). In the equation of motion m and γ are inertial and damping parameters respectively.

In this paper the incident field is assumed not to be very intense, which is fitting for FIR measurements as sources in this region are usually quite weak. Therefore only linear terms in Eq. (5) need to be considered, which can be done by linearizing in the small deviation from $P_0(z)$ due to the E field. Also, to avoid depolarization effects P_0 is taken to be in the plane of the film and is taken to lie along x. Writing $\vec{Q}$ for the deviation, the components of $\vec{P}$ are then $P_x = P_0(z) + Q_x$, $P_y = Q_y$ and $P_z = Q_z$. Expressions for the components of the variational derivative, $\delta F/\delta P_i$, $i = x, y$ or z then follow as in Ref. [3]. These can then be linearized by dropping terms in Q_i^2 or higher to give

$$C\frac{d^2\widetilde{Q}_j}{dz^2} + \left[m\left(\omega^2 - \omega_j^2\right) + i\omega\gamma\right]\widetilde{Q}_j + \widetilde{E}_j = 0 \tag{6}$$

where $m\omega_x^2 = A + 3BP_0^2(z)$ or $m\omega_j^2 = A + BP_0^2(z)$, $j = x$ or y. Here a single frequency ω has been assumed so that complex representations denoted $\widetilde{Q}_j$ and $\widetilde{E}_j$ can be used via $Q_j = (1/2)(\widetilde{Q}_j(z)e^{-i\omega t} + \widetilde{Q}_j^*(z)e^{i\omega t})$, and similarly for E_j. The relation complementary to Eq. (6) is the driven wave equation

$$\frac{d^2\widetilde{E}_i}{dz^2} + \epsilon_\infty\frac{\omega^2}{c^2}\widetilde{E}_i = -\frac{\omega^2}{\epsilon_0 c^2}\widetilde{Q}_i, \quad i = x, y \text{ or } z, \tag{7}$$

where ϵ_∞ accounts for the contribution of higher-frequency resonances to the dielectric response. For simplicity in this paper we will only consider x-polarization: $\vec{E} = (E_x, 0, 0)$, so that $\vec{Q} = (Q_x, 0, 0)$ and $\widetilde{E}_j = \widetilde{Q}_j = \omega_j = 0$, $j = y$ or z.

The complex optical reflection coefficient at frequency ω is found by solving Eqs. (6) and (7) for the fields in the film subject to electromagnetic boundary conditions—continuity of E and H—together with polarization boundary conditions (3) and (4). Assuming the metal to be of infinite conductivity implies that at the ferroelectric-metal boundary $z = -L$, $\widetilde{E}_x = 0$ and no wave is transmitted. The field in the ferroelectric at the incident surface $z = 0$ is matched to the incident and reflected waves. Because the ω_i involve the z-dependent $P_0(z)$, the solution of Eqs. (6) and (7) must in general be found numerically. For the bulk case when the boundaries are far away (or for the special case $\delta_1^{-1} = \delta_2^{-1}$) $P_0(z) = P_B =$ const. and the solution can be found analytically. Next we will look at the bulk modes for $C = 0$ before going on to the full numerical solution.

3 Polariton bulk modes

When $C = 0$ only the usual polariton mode propagates in the film. It is instructive to study the reflection coefficient for this case as it gives a qualitative picture of the influence of the damping parameter γ. With $C = 0$ Eqs. (6) and (7) show that $\widetilde{Q}_j \propto \widetilde{E}_j$ and the solution $\widetilde{E}_j \propto \exp(\pm qz)$, where $q_1^2 = \epsilon(\omega)\omega^2/c^2$ and

$$\epsilon(\omega) = \epsilon_\infty \frac{\omega_L^2 - \omega^2 - i\omega\gamma/m}{\omega_j^2 - \omega^2 - i\omega\gamma/m}, \qquad (8)$$

where $\omega_L^2 = \omega_j^2 + 1/\epsilon_0\epsilon_\infty m$. These $C = 0$ modes are the bulk polaritons, and in particular there is no propagating mode in the restrahlung region $\omega_j^2 < \omega < \omega_L^2$. These polariton solutions can be used for a film if it is assumed that there is no change in polarization near the surfaces so that $P_0(z) = P_B \; \forall z$ in the film. For a free standing film for which the wave incident from the vacuum side is $E_I \propto \exp(q_0 z)$, with $q_0 = \omega/c$, this implies that the magnitude of the reflection coefficient is 1 across the restrahlung, while outside of the region there is propagation into the film leading to a transmitted wave and a lowering of the magnitude from its maximum value of 1. However, here the incident wave is not only reflected in the restrahlung, but also outside of it due to the reflection at the ferroelectric-metal boundary. The reflection coefficient in this case may be calculated by applying the electromagnetic boundary conditions mentioned above and the result, when $\gamma = 0$, is $r = |r| = 1 \; \forall\omega$, and for $\gamma \geq 0$

$$r = -\frac{e^{2iqL}\left(\sqrt{\epsilon(\omega)} + 1\right) + \sqrt{\epsilon(\omega)} - 1}{e^{2iqL}\left(\sqrt{\epsilon(\omega)} - 1\right) + \sqrt{\epsilon(\omega)} + 1} \qquad (9)$$

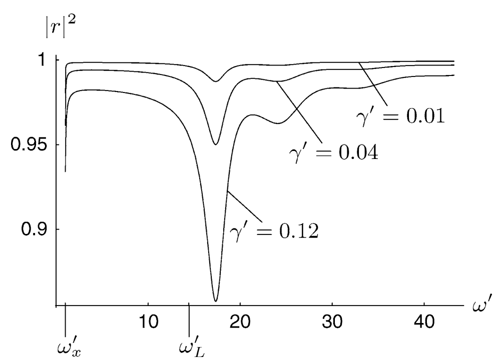

Fig. 1 Reflection coefficient for bulk polariton case. The following dimensionless variables have been used: $\gamma' = \gamma/\sqrt{maT_c}$, $\omega' = \sqrt{m/aT_c}$, where c is the speed of light; $L' = (L/c)\sqrt{aT_0/m} = 0.3\sqrt{2C_0}$ (corresponds to $L \approx 40$ nm; C_0 defined in Fig. 2; values for a and m are taken to be the estimated values for $BaTiO_3$in Ref. [4]). These definitions are for dimensionless temperature $t = T/T_0$, which is set at $t = 0.5$ and the value for $BaTiO_3$ of $T_0 = 401$ K is used for the plots in all the figures

Figure 1 shows plots of $|r|^2$ for various values of a dimensionless representation of γ for the metal substrate case; this representation and other dimensionless variables used are defined in the caption. For subsequent illustrations an estimate for $BaTiO_3$ of $\gamma' = 0.01$, taken from Ref. [4] will be used. It can be seen that the effect of damping is to reduce the reflectivity modulus across the restrahlung without producing interference fringes; these only become apparent outside of the region but then die away as the modulus moves towards 1. Overall the effect becomes more marked as the damping increases. In a free standing film ($\delta_1 = \delta_2 = \delta$) it has been shown [4] that the presence of $C \neq 0$ modes causes fringes to appear across the restrahlung and furthermore the effect is distinguishable from the effect of $\delta^{-1} \neq 0$ values that lead to a z dependent polarization $P_0(z)$. So the question now is what is the nature of these size effects when a metal substrate is present, and is useful information about them still obtainable from reflection measurements in the terahertz region? To address this we will proceed straight to the numerical calculation.

4 Numerical calculation

With $C, \delta_1^{-1}, \delta_2^{-1} \neq 0$, $P_0(z)$ is given by elliptic functions [5] and the solution of Eqs. (6) and (7) must be performed numerically. We will use the following notation to describe the fields in the vacuum and film, remembering that only x-polarization is being considered:

$$\widetilde{E}_x(z) = \begin{cases} \widetilde{E}_I e^{-iq_0 z} + \widetilde{E}_R e^{iq_0 z} & \text{if } z > 0, \\ \widetilde{E}_F(z) & \text{if } -L < z < 0. \end{cases} \qquad (10)$$

The aim is to calculate the reflection coefficient $r = \widetilde{E}_R/\widetilde{E}_I$. Since there is no analytic expression for $\widetilde{E}_F$ it is necessary to integrate Eqs. (6) and (7) across the film. Following the method of Chew et al. [4] it is best to start the integration from $z = -L$, since there are no waves propagating in the metal. The prescribed boundary conditions are

$$\widetilde{E}_F(-L) = 0 \text{ (infinite conductivity in metal)}, \qquad (11)$$

$$\left(d\widetilde{Q}_x/dz - \widetilde{Q}_x/\delta_1\right)_{z=-L} = 0 \text{ (bound. cond. (3))}, \qquad (12)$$

$$\widetilde{E}_F(0) = \widetilde{E}_I + \widetilde{E}_R = (1 + r)\widetilde{E}_I$$
$$\text{(continuity of } \widetilde{E}_x \text{ at } z = 0), \qquad (13)$$

$$d\widetilde{E}_F/dz|_{z=0} = -iq_0(\widetilde{E}_I - \widetilde{E}_R) = -iq_0(1 - r)\widetilde{E}_I$$
$$\text{(continuity of } \widetilde{H}_y \text{ at } z = 0), \qquad (14)$$

$$\left(d\widetilde{Q}_x/dz + \widetilde{Q}_x/\delta_2\right)_{z=0} = 0 \text{ (bound. cond. (4))}. \qquad (15)$$

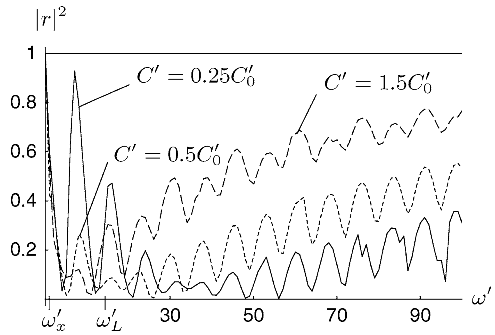

Fig. 2 Effect of varying $C' = C/c^2m$ relative to $C'_0 = 0.00475$, the dimensionless value calculated from the estimates for $BaTiO_3$ of C and m in Ref. [4]. The film thickness expressed in dimensionless form is taken to be $L' = 0.3\sqrt{C'_0}$, and $t = 0.5$. Dimensionless frequencies ω'_x and ω'_L are scaled in the same way as ω', defined in Fig. 1

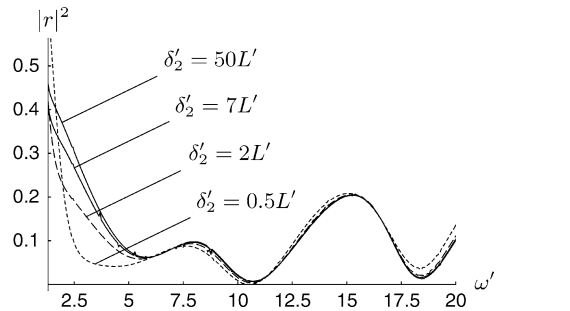

Fig. 3 The effect of varying dimensionless extrapolation length $\delta'_2 = (\delta_2/c)\sqrt{aT_0/m}$ at $t = 0.5$, with all other parameters for $BaTiO_3$ as given in Figs. 1 and 2

These five boundary conditions are sufficient for solving the problem: four are needed since Eqs. (6) and (7) are two coupled second-order equations the solution of which requires four boundary conditions; a further condition is required to find r. The values of $\widetilde{E}_F(0)$ and $(d\widetilde{E}_F/dz)_{z=0}$ are found by integrating Eqs. (6) and (7) from $z = -L$ to 0; r can then be found by eliminating $\widetilde{E}_I$ from Eqs. (13) and (14).

Since the required boundary conditions are not all prescribed at the same point the numerical solution of Eqs. (6) and (7) is a boundary value rather than initial value problem. To deal with this these two equations were expressed as four first order differential equations (ODEs)—a standard step in the solution of coupled ODEs. Next, rather than working further with complex variables for the numerics, the four coupled ODEs along with boundary conditions Eqs. (11) and (15) were split into real and imaginary parts; the resulting eight ODEs all in real variables, were then solved using routines newt and shoot from Ref. [8] which implement shooting and Newton-Raphson methods. Once the numerical integration of Eqs. (6) and (7) is complete, it is easy to reconstruct the complex values for the calculation of r.

The numerical results of the calculation are presented as graphs of $|r|^2$ versus ω' for various values of dimensionless representations, C', δ'_1 and δ'_2 (defined in Figs. 1 and 2), of the size effect parameters. Figure 2 shows the influence of varying C'. It can be seen that this effect is noticeable beyond the restrahlung region $1 < \omega' < 14.1$, but the changes within this region are more pronounced. It is obvious from Fig. 2 that fringes do appear now that $C \neq 0$ modes are present.The dramatic, close to zero drop in reflection at lower frequencies is caused by good impedance matching of these to the film [3], so that very little is reflected at the vacuum-ferroelectric boundary and the wave reflected from the metal at the opposite boundary interferes constructively with the wave transmitted to the film from the vacuum. At higher frequencies the impedance matching is not so strong [3]; consequently more of the incident wave is reflected from the vacuum-ferroelectric boundary and the drop in reflection lessens as ω' increases.

Figure 3 shows the effect of varying δ'_2, the representation of the extrapolation length at the ferroelectric-metal boundary, relative to a fixed δ'_1 value. This mainly influences the first part of the restrahlung with changes at higher frequencies less pronounced. Thus the effect is more localized in frequency than that of changes in C'. This is not surprising since C enters the equations more pervasively than δ_2, which only appears in boundary condition (4).

Overall, especially because of the appearance of fringes across the restrahlung, the reflection curves in Figs. 2 and 3 show that the influence of the size effects is quite distinct from the influence of damping. Also the individual effect of changing C' and δ_2 are distinguishable. The restrahlung region which is in the FIR, is the most sensitive to these changes. This suggests that FIR reflection measurements would be a sensitive probe of size-effects in a ferroelectric film on a metal substrate. Furthermore, comparison with the reflection curves characteristic of free standing films in Ref. [4] in which there is a hill across the restrahlung with fringes superposed rather than the dip with fringes illustrated here. So the metal substrate gives a very distinctive signature to the reflection curves.

5 Conclusion

According to the model calculations here rooted in LDG theory, terahertz wave reflection measurements ought to be a sensitive probe of size effects in ferroelectric thin films on metal substrates. This is of use, for example, because in a typical memory application metal electrodes may be attached to the ferroelectric. The FIR restrahlung region would be the most sensitive; however, particularly for changes in C', higher frequencies are also noticeably affected.

The character of the reflection curves here has been shown to be of a very different character to curves for free-standing films previously studied. This suggests the possibility that the reflection measurements may also be sensitive to how well the substrate is bonded to the ferroelectric: the presence of air gaps might have a large influence on measurements. After further study this might result in a useful nondestructive testing technique.

Other future work could include the obvious extension of treating the metal more realistically by taking into account the penetration of radiation to a skin depth. Such work is in progress using the well-known Drude model of electrons in a metal.

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